Manufacture of specific structure of aluminum-doped zinc oxide films by patterning the substrate surface

X. Jiang[a)]
Fraunhofer-Institut für Schicht- und Oberflächentechnik, Bienroder Weg 54E, D-38108 Braunschweig, Germany

C. L. Jia
Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

B. Szyszka
Fraunhofer-Institut für Schicht- und Obserflächentechnik, Bienroder Weg 54E, D-38108 Braunschweig, Germany

(Received 4 December 2001; accepted for publication 26 February 2002)

(0001)-oriented aluminum-doped zinc oxide films were prepared using a magnetron sputtering technique. High-resolution transmission-electron-microscopic images show that the oriented grains nucleate directly on the substrate surface and grow with equal lateral dimensions through the film thickness. A surface-energy-driven self-texture mechanism was proposed on the basis of process modes. A method for manufacturing specific film structure by patterning the substrate surface is tested and discussed. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1473683]

Zinc oxide (ZnO) has a hexagonal wurtzite structure. If it is doped with a suitable metallic element like aluminum a multifunctional material can be prepared which is not only highly transparent in the visible optical spectral region but also has metal-like electrical conductivity. ZnO films are therefore a key material for numerous high-tech industrial applications, e.g., as transparent electrodes for photovoltaics, flat panel displays and for energy-efficient or smart coatings on architectural glazing.[1–5] Due to its piezoelectric properties, ZnO film is also a good candidate for surface acoustic wave (SAW) devices that are used as electronic signal filters for mobile telecommunications. If a thin *c*-axis textured ZnO films is deposited on a material like diamond, a high-frequency (>3 GHz) SAW device can be prepared.

The difficulty in depositing a thin, *c*-axis-oriented film of high quality is control of film nucleation and the initial growth process. For the preparation of ZnO films both physical vapor deposition, such as rf and dc sputtering,[6–8] ion plating,[9] and pulsed laser evaporation,[10,11] as well as chemical vapor deposition (CVD)[12,13] have been used. Recently, the reactive midfrequency (MF) magnetron sputtering technique has been developed. Promising results have been obtained for ZnO:Al films. Films deposited at 200 °C substrate temperature with a deposition rate of up to 9 nm/s exhibit a low resistance of 300 $\mu\Omega$ cm. Furthermore, they are more stable in reducing ambient than other transparent conductive oxide (TCO) materials[14] and their surface topography can be modified by etching,[15] which makes them very attractive for photovoltaic applications.

The heteroepitaxial growth of ZnO on a substrate such as sapphire is relatively well understood.[16] Experimental methods have also been developed for *c*-axis-oriented ZnO nucleation on other substrates (amorphous materials).[17] Microscopic investigation of ZnO films showed that, for a large range of deposition parameters, preferred film orientation with the *c* axis perpendicular to the substrate surface can be achieved.[18] A nanocrystalline random composite region, which is often combined with amorphous phases at the grain boundaries, has been observed in the vicinity of the interface before columnar grains are formed.

Here we present direct high-resolution transmission electron microscopy (HRTEM) evidence that a highly (0001)-textured ZnO:Al film structure can be generated directly on nucleation sites via MF magnetron sputtering. In contrast to previously established mechanisms of film texture formation in a vapor deposition process, the texturing of our ZnO:Al films is neither dependent on the substrate structure, nor on the grain evolution selection during film growth. A surface-energy-controlled step-flow scheme was proposed, which is related to the process modes.

ZnO:Al samples were prepared by MF magnetron sputtering at a power density of approximately 8 W cm^{-2}. Homogeneous metallic targets with a 1.5 wt % Al concentration were used. Two sets of samples were prepared in metallic and transition sputtering modes, respectively, by controlling the oxygen partial pressure and plasma power density.[19] The experimental parameters are given in Table I. All films were deposited at a fixed target-to-substrate distance of 90 mm and at a constant argon pressure of 1.2 mTorr. The base pressure was lower than 3×10^{-6} Torr for all experiments.

The Al doping levels were evaluated by electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS), and showed a homogeneous Al doping content of 2.5%, independent of the O_2 partial pressure. Within the detection limit of EPMA, impurity incorporation of Si, C, N and Na was observed for concentrations below 0.1 at. %. Optical and electrical characterizations were performed by spectrophotometry in the spectral range of 250–2500 nm and by Hall measurements taken at room temperature using the van der Pauw method. The films have no light absorption in the visible spectral range and the electrical resistance exhib-

a)Electronic mail: jiang@ist.fhg.de

TABLE I. Parameters for reactive MF magnetron sputtering of ZnO:Al layers in metallic and transition modes.

Deposition mode	Transition mode	Metallic mode
Target	Homogeneous: $c_{Al}=1.5$ wt %	Homogeneous: $c_{Al}=1.5$ wt %
O_2 partial pressure	0.15 mTorr	0.25 mTorr
Total pressure	1.35 mTorr	1.45 mTorr
Power	4.5 kW	3.5–5.5 kW
Target voltage	430 V	360 V
Target–substrate distance	90 mm	90 mm
Substrate temperature	150 °C	150 °C
Substrate material	Si, quartz, borosilicate glass	Si, quartz, borosilicate glass
Deposition rate	3–4 nm/s	3–4 nm/s
Deposition time	120 s	170 s

its only 400 $\mu\Omega$ cm for the films sputtered in metallic mode. Crystallographic structures of the films were investigated by x-ray diffraction (XRD), and showed a highly *c*-axis-film texture in metallic mode.

The interface structure between the ZnO film and the silicon substrate was investigated by HRTEM. In order to avoid the influence of the epitaxial effect of the silicon wafer the native surface oxide layer was not removed. A high-resolution cross-sectional lattice image of the interface is shown in Fig. 1(a). By viewing the image at glancing angle along the interface, it becomes obvious that all the ZnO crystallites initially formed on the thin amorphous SiO_2 native layer oriented themselves with their (0001) planes parallel to the substrate surface, forming a nearly perfect *c*-axis-textured columnar structure at the interface. No secondary phases such as Al_2O_3 and amorphous ZnO are recognized at the grain boundaries. Figure 1(b) shows a single column with a diameter of about 30 nm from the interface to the top region of the film.

The lattice images shown in Fig. 1 provide us with strong evidence that strictly *c*-axis-oriented ZnO:Al crystals can be grown on a silicon wafer in spite of the amorphous native surface SiO_2 layer, i.e., without the influence of epitaxial growth. This leads to the conclusion that the film crystal orientation is not affected by the crystallographic structure of a substrate, but is a result of a self-ordering effect caused by the minimization of the crystal surface free energy as well as by the interaction between the deposit material and the substrate surface. This crystallization phenomenon is often called self-texturing.

In general, textured film growth can be realized either by an evolution competition process of the statistically oriented grains or by a particle flux-determined selective growth process. In the former case, the so-called van der Drift mechanism, only grains with their fastest crystal growth direction parallel to the film growth direction can survive while other grains will be overgrown. In the latter case grains with a certain special orientation will be allowed to grow by ion impact while the growth of other grains will be suppressed due to a selective ion etching or resputtering process. In our film growth the van der Drift mechanism can be ruled out due to the fact that all the initial ZnO crystallites are oriented and form a columnar structure and no crystallites were overgrown during the growth process. In contrast to ion beam sputtering, no strictly oriented ion beam flux is available in the MF magnetron sputtering process, especially if no substrate bias potential is applied, as in our experiment. Therefore a different mechanism, surface energy driven growth of *c*-axis ZnO, must be considered to interpret the phenomenon observed.

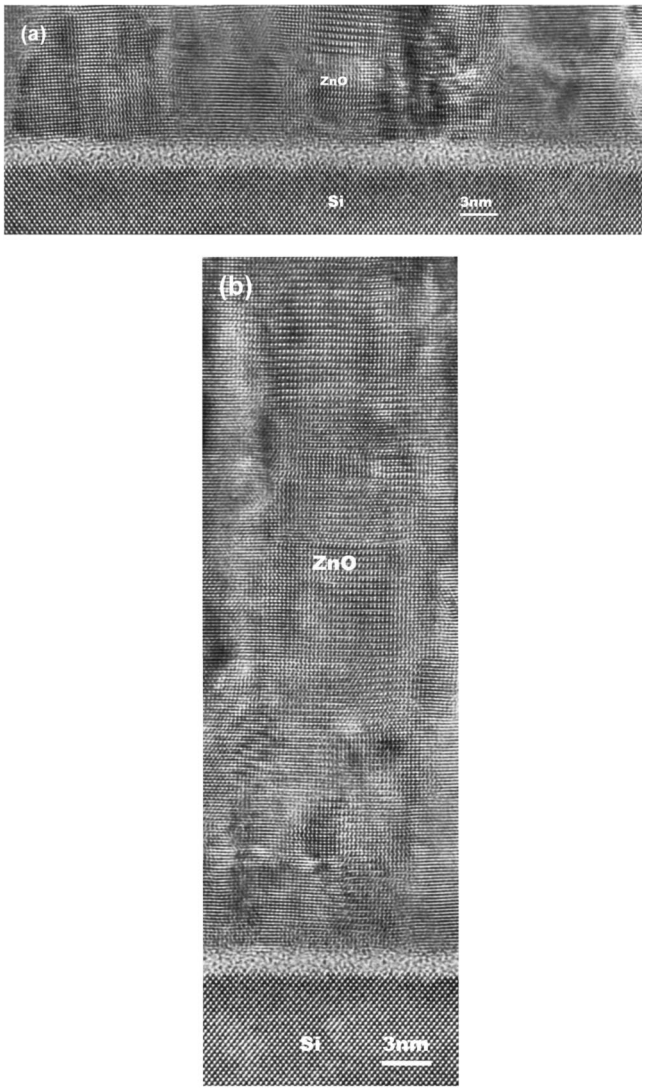

FIG. 1. Lattice image of (a) the interface between ZnO:Al and silicon and (b) a single ZnO:Al columnar grain. The micrographs were taken along the [110]-zone axis of silicon crystals.

According to the Wulff theorem, which was described in great detail by Winterbottom,[20] the dominant crystal faces are those with the smallest surface energy. The crystal faces with the lowest free energy have a tendency to grow parallel to the substrate. This tendency strongly increases with an increase in cohesive energy of the film to the substrate. Since the (0001) faces of ZnO have the lowest free energy [1.6 J/m^2 for (0001), 2.0 J/m^2 for $(11\bar{2}0)$, and 3.4 J/m^2 for $(10\bar{1}0)$, respectively],[17] they will try to grow parallel to the silicon surface if the process parameters are adjusted so that deposition occurs at thermodynamic equilibrium.

In fact, self-texturing of a film may lead to a similar film structure as that by the particle-flux-determined selective growth process. The difference between the two processes is, however, that in the latter case the columnar axis of film grains is parallel to the ion flux while the self-texture is independent of the ion flux direction. To confirm the proposed

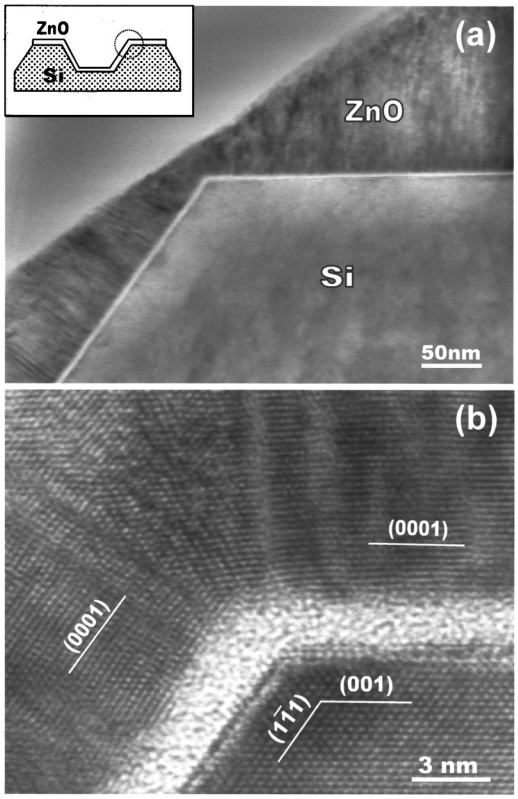

FIG. 2. Low magnification image (a) and a lattice image (b) of ZnO:Al film deposited on a patterned Si surface, confirming the Si surface-controlled ZnO:Al film orientation.

mechanism and to exploit a practical application of the self-texturing effect a test experiment was performed in which we employed a substrate with different surface planes obtained by wet chemical etching, shown in Fig. 2(a). The ZnO film was deposited and the interface structure at the surface plane edges was studied by HRTEM. It is clearly seen that the ZnO (0001) planes really do grow over the surface edges and parallel to the substrate surface [Fig. 2(b)]. The ion flux effect can therefore be ruled out.

As is demonstrated in Fig. 2, the self-texturing process can provide us with a method by which to design and manufacture film microstructure which is of crucial importance for specific electronic and optical applications. Using a specially patterned substrate we can define the grain size, surface morphology and the roughness of the deposited films for photovoltaic technology. The *c*-axis orientation of the film crystallites can be controlled in local areas on a microscale and has potential applications in microsystem techniques due to the isotropic piezoelectricity properties of ZnO and in the fabrication of ZnO thin film transistors.[21]

The self-texture control is based on the equilibrium state of the deposition. The conditions at the sputtered target are mainly determined by the power density and the partial pressure of the reactive gas. With a constant reactive gas flow the plasma discharge can be operated in elemental (metallic) mode or in reactive mode (oxide).[22] In metallic mode metal sputtering occurs and the target remains free of reaction products. In reactive mode the target is completely covered with reaction products. Sputtering of the reaction products and their atomic components takes place generally with a very low sputtering yield. The discharge voltage and current differ from those in metallic mode. Within the transition region between the two modes the degree of coverage of the target surface changes continuously mainly as a function of the reaction gas partial pressure. This so-called transition mode proves to be of significance for attaining specific film properties and high deposition rates.

Our *c*-axis-oriented ZnO films were obtained in metallic mode (see Table I) which should be in a more equilibrium state. By reducing the oxygen partial pressure and adjusting the power density ZnO films were also deposited in transition mode (Table I). In comparison to the *c*-axis-textured film sputtered in metallic mode the film deposited at transition mode shows random orientation at the beginning of film formation. The (0001) crystal planes of the ZnO crystallites are no longer *c* axis oriented and the film does not show any columnar film structure.

In summary, self-texturing of transparent and conductive ZnO:Al films was demonstrated by a HRTEM investigation of the interfaces. The growth of *c*-axis-oriented wurtzite phase is already favored in the nucleation stage due to minimization of the surface energy which is strongly affected by the sputtering modes of Zn:Al targets. Thus, *c*-axis-oriented polycrystalline films are grown, even for processes with weak ion bombardment and low substrate temperature. The self-texturing process enables us to design and manufacture a film microstructure for specific electronic and optical applications and for microsystem techniques.

The authors would like to thank R. Debusmann for film preparation and K. Urban for fruitful discussions.

[1] T. Yamamoto, T. Shiosaki, and A. Kawabata, J. Appl. Phys. **51**, 3113 (1980).
[2] C. Beneking, B. Rech, S. Wieder, O. Kluth, H. Wagner, W. Frammelsberger, R. Geyer, P. Lechner, H. Rubel, and H. Schade, Thin Solid Films **351**, 241 (1999).
[3] Y. Akao, and T. Haranoh, Proceedings of the 2nd ICCG, 1998, p. 338.
[4] I. Hamberg and C. G. Granqvist, J. Appl. Phys. **60**, R123 (1986).
[5] G. Granqvist, Appl. Phys. A: Solids Surf. **57**, 19 (1993).
[6] D. L. Raimodi and E. Kay, J. Vac. Sci. Technol. **7**, 96 (1970).
[7] F. S. Hickernell, J. Appl. Phys. **44**, 1061 (1973).
[8] S. Jäger, B. Szyszka, J. Szczyrbowski, and G. Bräuer, Surf. Coat. Technol. **98**, 1304 (1998).
[9] K. Machida, M. Shibutani, Y. Murayama, and T. R. Matsumoto, Trans. Inst. Electron. Commun. Eng. Jpn. **62**, 354 (1979).
[10] J. Exarhos and S. K. Sharma, Thin Solid Films **270**, 27 (1995).
[11] J. S. Zabinski, J. Corneille, S. V. Prasad, N. T. McDevitt, and J. B. Bultmann, J. Mater. Sci. **32**, 313 (1997).
[12] T. Shiosaki, S. Ohnishi, and A. Kawabata, J. Appl. Phys. **50**, 3113 (1979).
[13] C. Galli and J. E. Cooker, Appl. Phys. Lett. **16**, 439 (1970).
[14] T. Minami, H. Sato, H. Nanto, and S. Takata, Thin Solid Films **176**, 277 (1989).
[15] O. Kluth, B. Rech, L. Houben, S. Wieder, G. Schope, C. Beneking, H. Wagner, A. Loffl, and H. W. Schock, Thin Solid Films **351**, 247 (1999).
[16] V. Srikant, V. Sergo, and D. R. Clarke, J. Am. Ceram. Soc. **78**, 1931 (1995).
[17] N. Fujimura, T. Nishihara, S. Goto, J. Xu, and T. Ito, J. Cryst. Growth **130**, 269 (1993).
[18] N. Wanderka, I. Urban, I. Dorfel, E. Schierhorn, F. Fenske, and W. Fuhs, Thin Solid Films **330**, 108 (1998).
[19] B. Szyszka, Thin Solid Films **351**, 164 (1999).
[20] W. L. Winterbottom, Acta Metall. **15**, 303 (1967).
[21] D. C. Look, Mater. Sci. Eng., B **80**, 383 (2001).
[22] S. Schiller, G. Beister, and W. Sieber, Thin Solid Films **111**, 259 (1984).